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MEMORANDUM FOR PRS (In-House Publication)

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SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2003-130**
Jerry Boatz (AFRL/PRSP) et al., "First Principles Calculations of the Interaction of Nitro Compounds with the Al (111) Surface"

DoD High Performance Computing Users Group Conf. **(Statement A)**
(Bellevue, WA, 9-13 June 2003) (Deadline = 09 June 2003)

First Principles Calculations of the Interaction of Nitro Compounds with the Al (111) Surface

DoD UGC, 9-13 Jun 03

Bellevue, WA

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Multiscale Simulations of High Energy Density Materials (MSoH) Challenge Project

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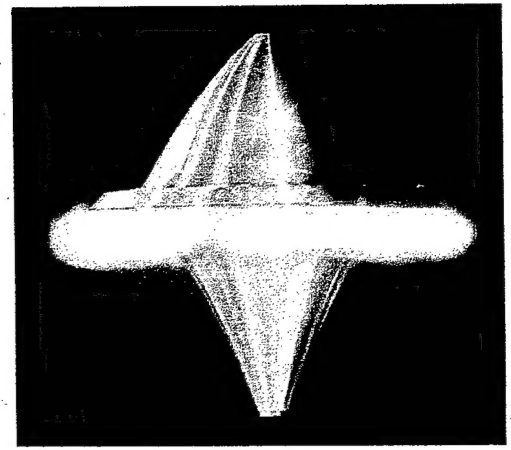
OUTLINE

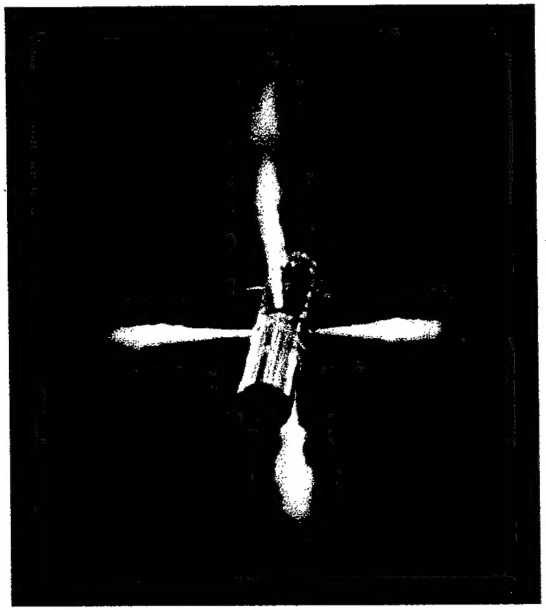
1. Introduction
   - Background on HEDM
   - Payoffs
2. Theoretical Methods and benchmarks
   - Plane-wave DFT
   - Molecular Dynamics
3. Results
4. Summary

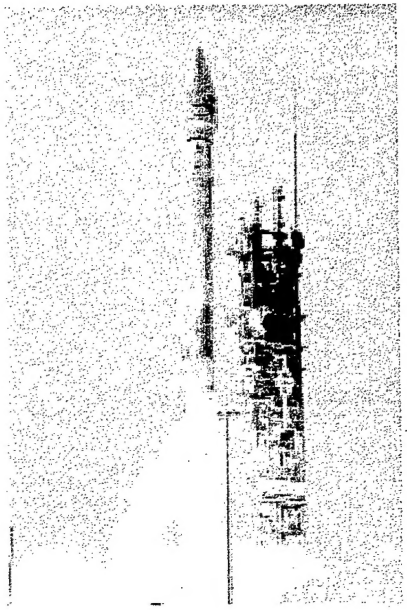
What We Are Trying To Do

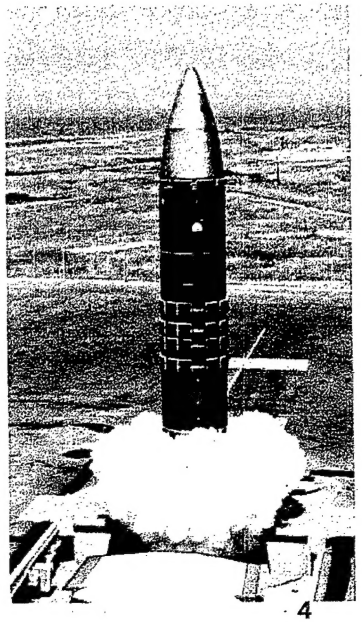
Identify, develop, and transition new propellants and advanced concepts for propulsion applications

- Hydrocarbon fuels for liquid boost
- Liquid & solid oxidizers for boost and upper stages
- Monopropellants for spacecraft and upper stages
- Laser lightcraft for microsatellite and other applications









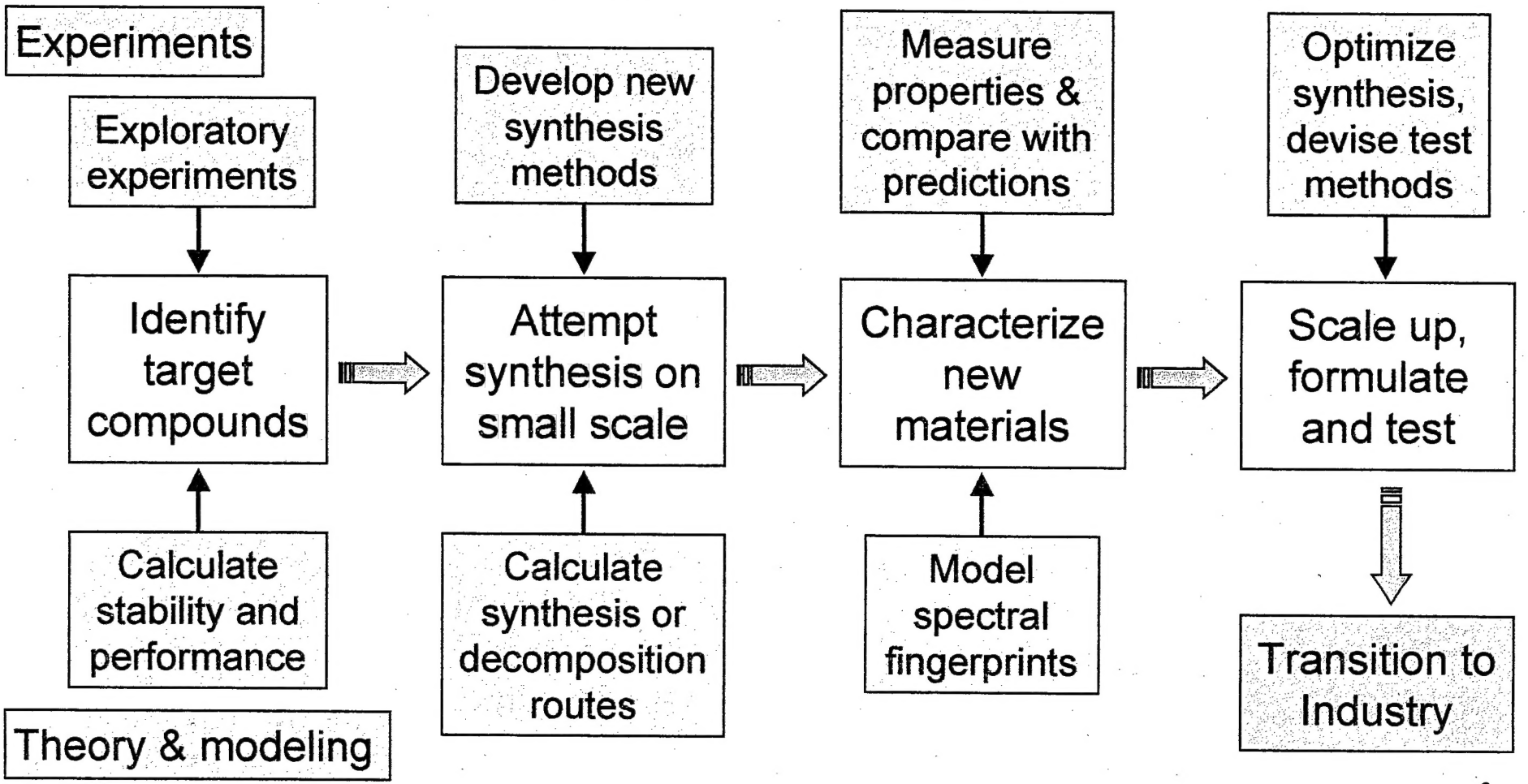
What Difference It Will Make

Vehicle Type	Baseline Vehicle	Propellant	Takeoff Mass (lb)	Payload Mass (lb)	Payload Mass (lb) With 10% Isp Increase
Two-stage ELV	Atlas II // Centaur D-1A	RP-1/LOX (Isp = 295 s) // LH2/LOX (Isp = 455 s)	360,000	12,500	15,600 (+25%)
SSTO RLV	Lockheed SSTO	LH2/LOX (Isp = 455 s)	1,900,000	40,000	68,000 (+70%)
Missile Defense Interceptor	Boost-Phase Interceptor	HTPB/Al/HMX (Isp = 270 s)	1,847	74	110 (+49%)

Our research is aimed at increasing propellant Isp by as much as 50%

How We Do What We Do
Propellant Discovery & Development

Employ a synergic blend of experimental, theoretical, and computational techniques derived from the disciplines of chemistry and physics



MSoH: Concept

Atomistic level understanding of condensed phase properties of energetic materials

- which factors influence the phase transitions (e.g., the melting point of energetic crystals?
- what is the mechanism of phase stabilization in AN salts?
- how are the chemical properties of energetic materials influenced by chemisorption on metallic surfaces?

Technical tasks include

a) Characterization of static, dynamic properties of AN, ADN salts
   - structural, thermodynamic, transport properties and phase transitions

b) Investigation of KNO_3-induced phase stabilization of ammonium nitrate (AN) salts

c) Interactions between HEDM molecules and Al surfaces, nanoclusters.
   - how do surface/cluster interactions modify the chemical properties of HEDM?
   - RDX, HMX, FOX-7 (1,1-diamino-2,2-dinitroethylene)

Objectives of the Current Computational Research Program

To identify the chemisorption mechanism of various nitro compounds on Al surface.

Particular important goals:

a) to clarify if dissociative chemisorption can take place;

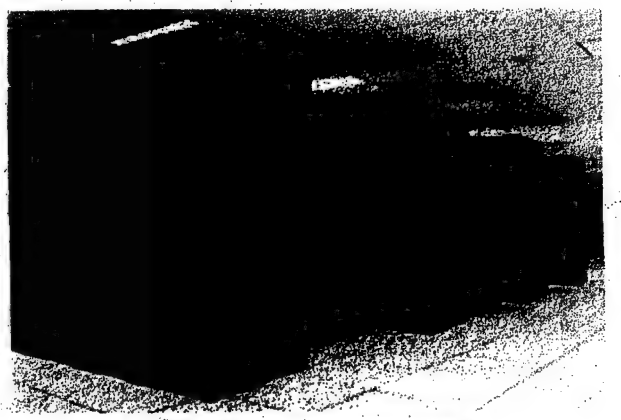
b) what type of species or radicals are formed on the surface.

Limitations: temperature effects are not considered in the present set of calculations.

Computational Method :
Ab Initio Total Energy Calculations

- **Theoretical approach: spin polarized DFT with GGA and pseudopotential method.**
- **The occupied electronic orbitals are expanded in a plane-wave basis** $\Psi_i(r) = \sum_G c_{iG} \exp(iGr)$ **with reciprocal lattice vectors G limited by** $\frac{\hbar^2 G^2}{2m} < E_{cut}$ **, Ecut: 395 eV**

  Exchange-Correlation Functionals: PW91
- **Pseudopotentials: Ultrasoft Vanderbilt-type**
- **K-point sampling: Monkhorst-Pack Special K-pts**
- **Electron Smearing Near Fermi Level with Extrap.to T=0**
  VASP: Methfessel-Paxton Function, 0.2 eV min. width.



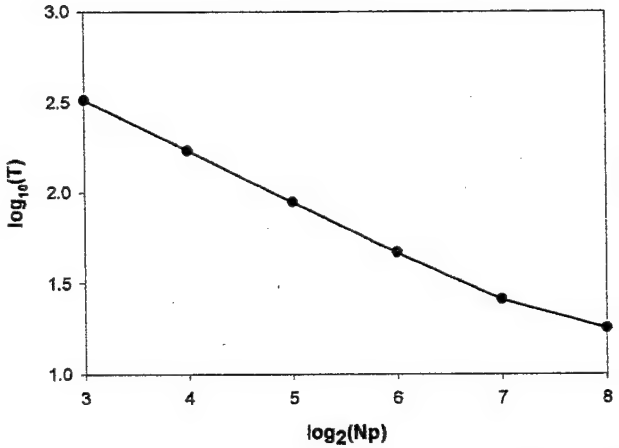
VASP: "Vienna Ab Initio Simulation Package",
J. Haffner, G. Kresse et al., Univ. of Vienna

ARL, ASC, and ERDC MSRCs

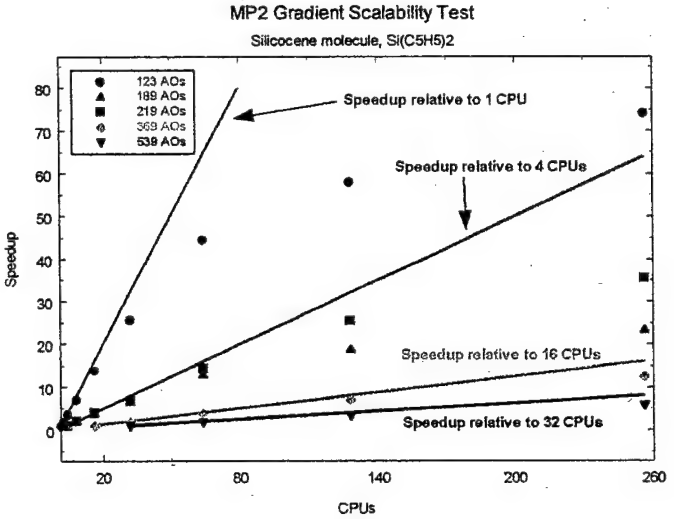
MSoH: Scalable CCM Software

DL_POLY_2.0

Run on Cray T3E

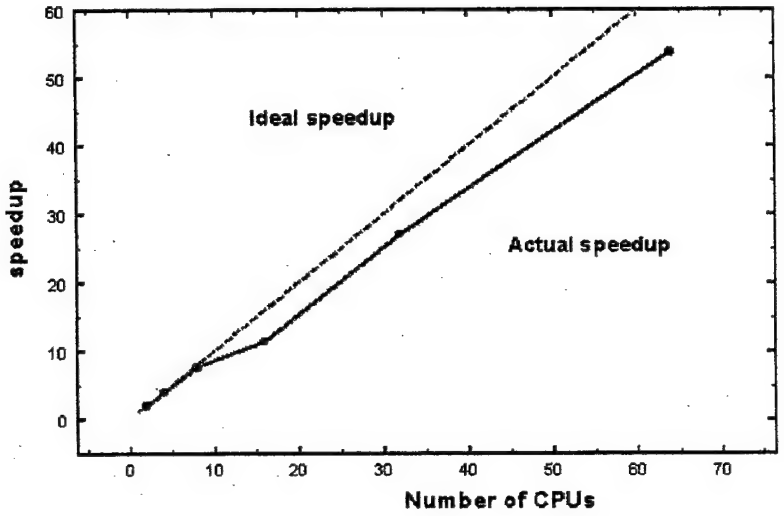


GAMESS

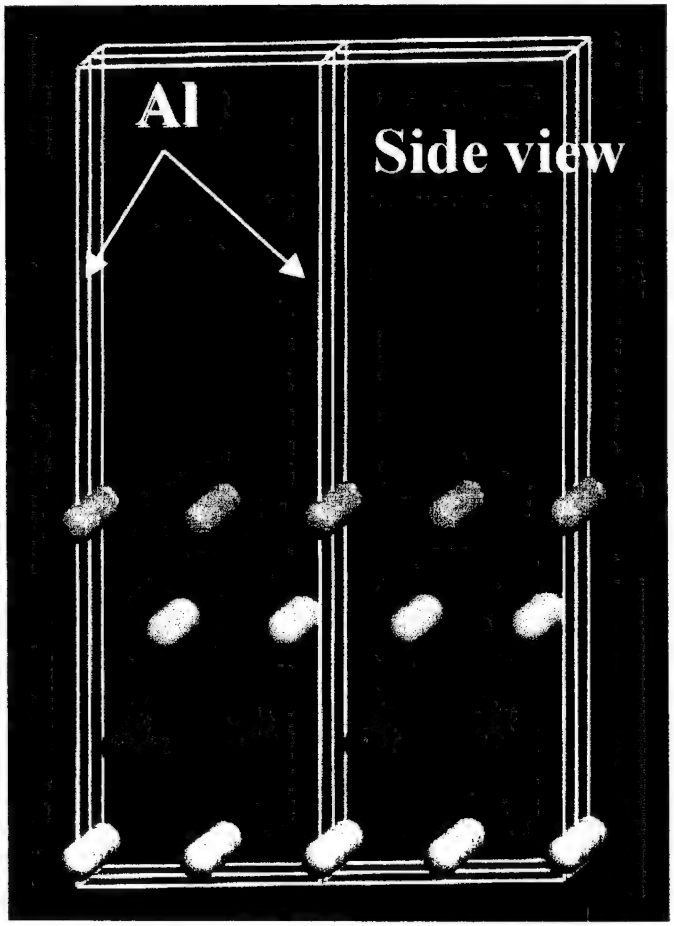


CASTEP

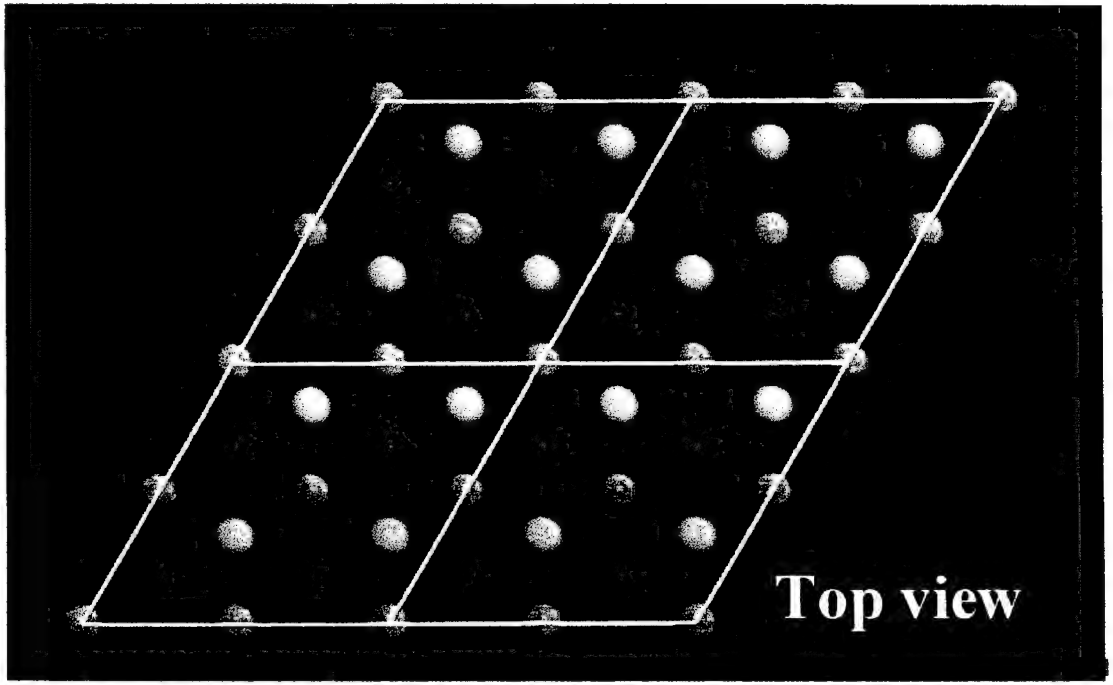
Run on SGI O3K



Al(111) Slab Model



Al(111)- (3x3) surface units slab model with 4 layers (36 Al atoms), 3D periodic boundary conditions



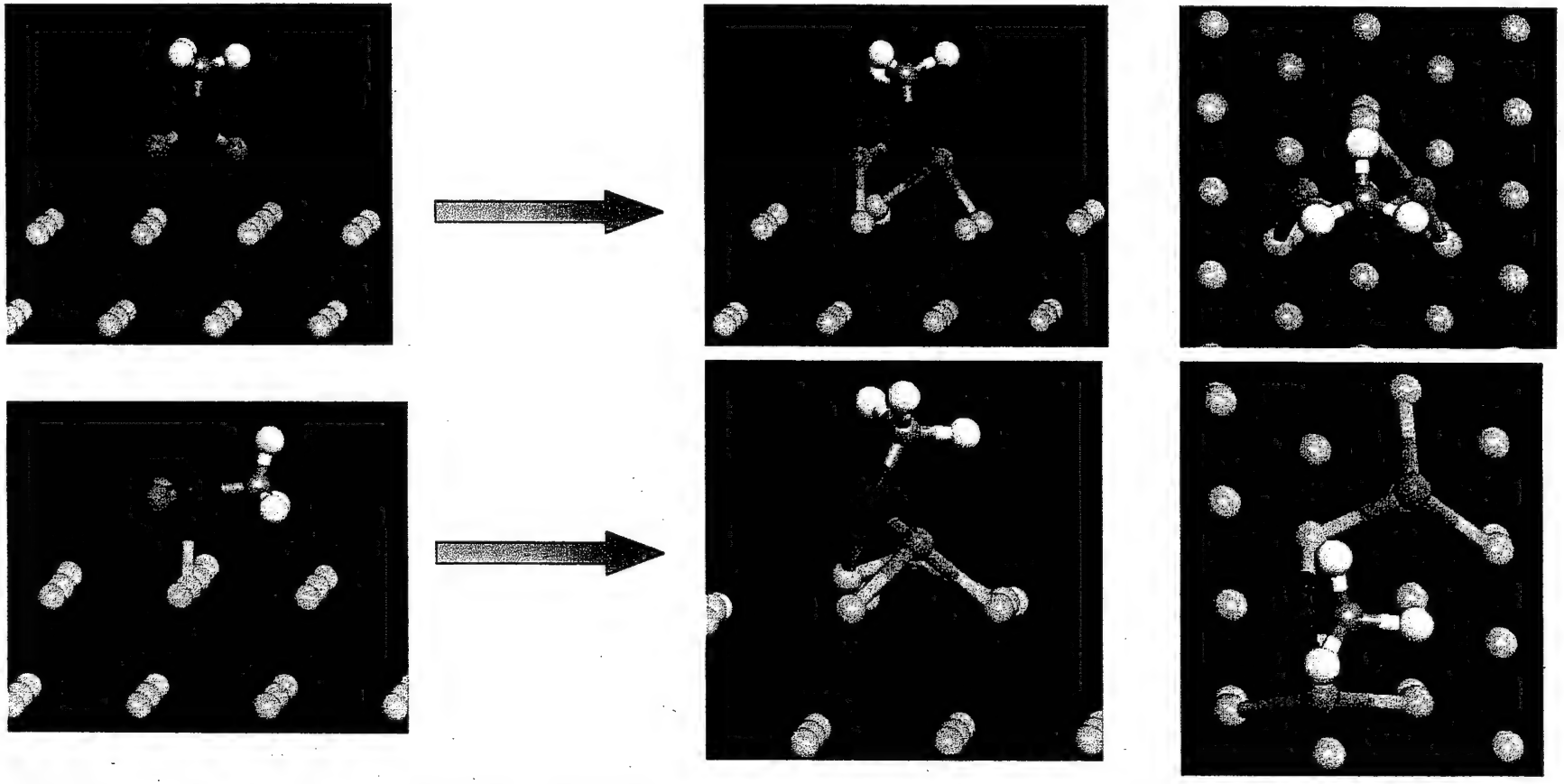
Chemisorption of Nitromethane on Al(111)

Initial configuration

Optimized configuration

side view

top view



Formation of strong Al-O bonds; deformations of NM molecule

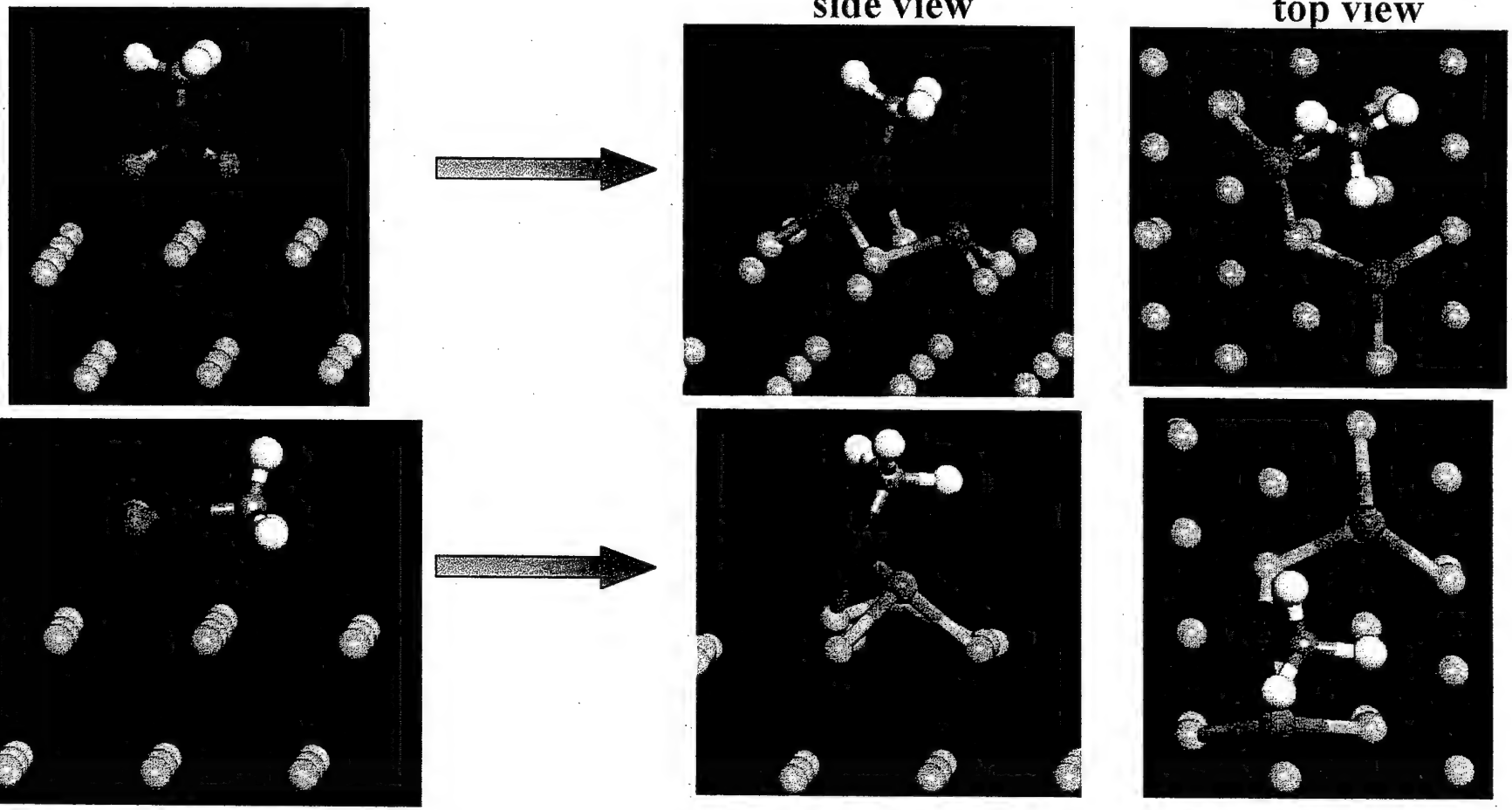
Dissociative Chemisorption of Nitromethane

Initial configuration

Optimized configuration

side view

top view



*** Dissociation of one O atom, oxidation of Al surface atoms.**

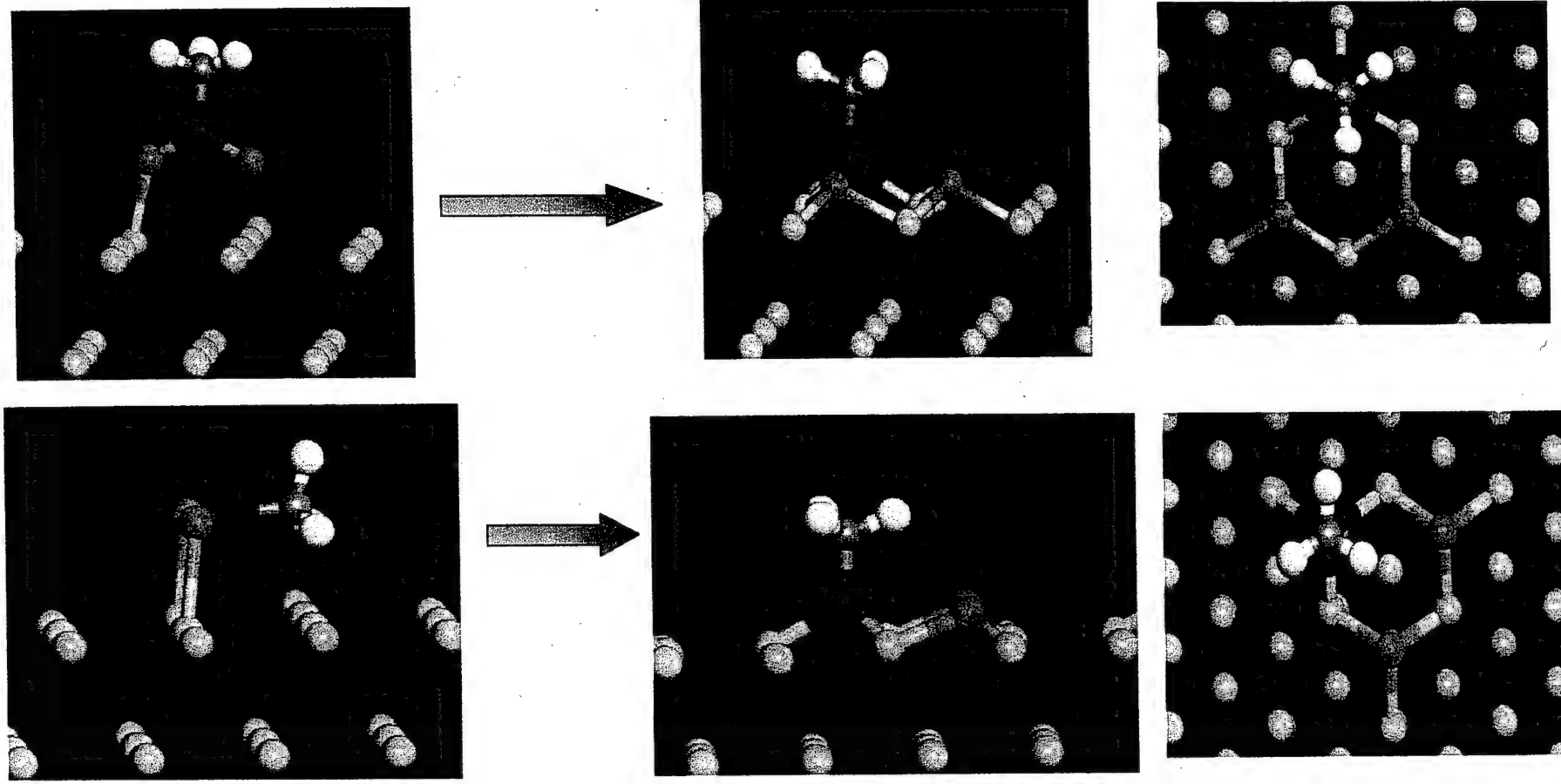
Dissociative Chemisorption of Nitromethane

Initial configuration

Optimized configuration

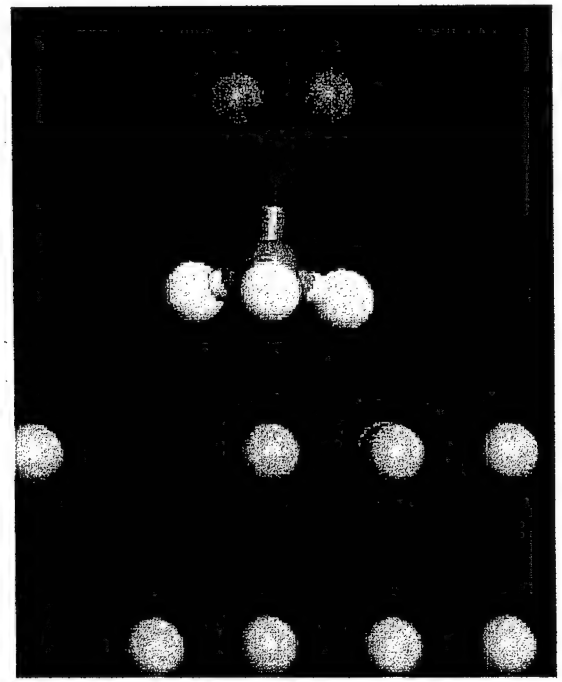
side view

top view

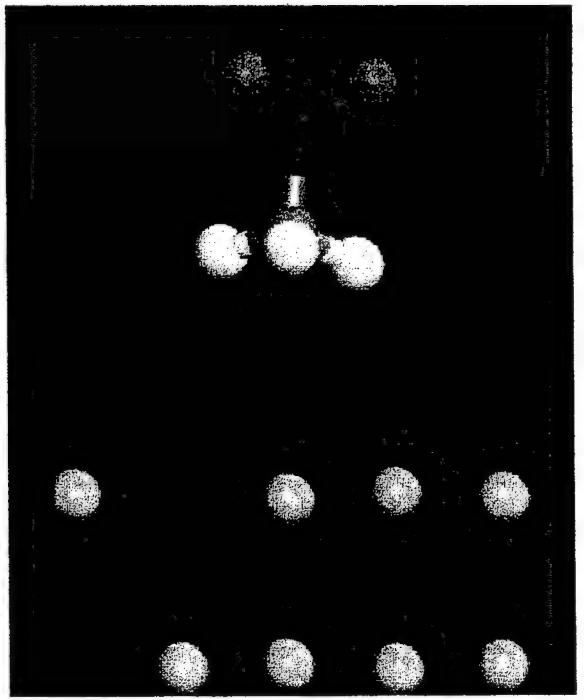


*** Dissociation of both O atoms, oxidation of Al surface atoms.**

There are some initial configurations for which nitromethane does not chemisorb

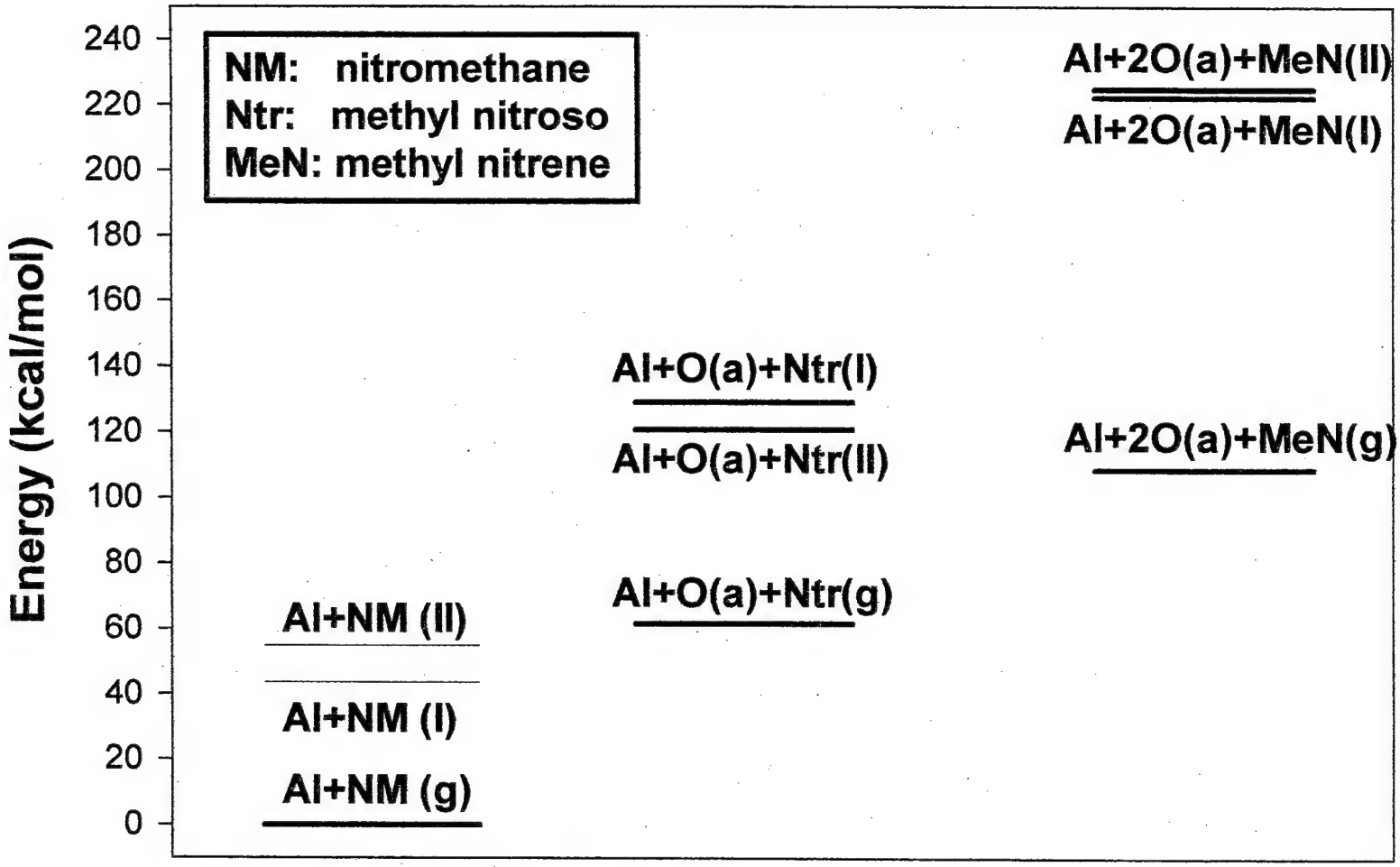


Initial configuration



Final configuration

Adsorption Energies of Nitromethane



Chemisorption of FOX-7 on Al(111)

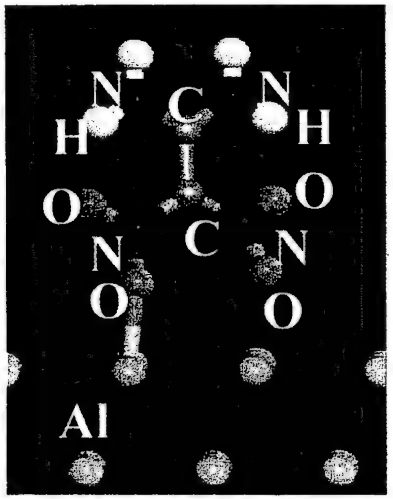
$(NH_2)_2C=C(NO_2)_2$

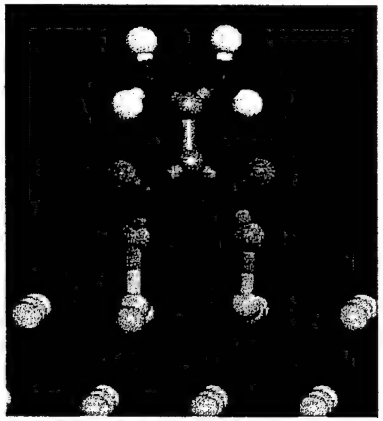
Initial configuration

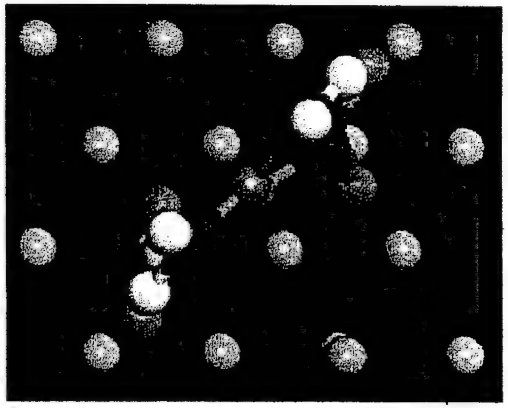
Optimized configuration

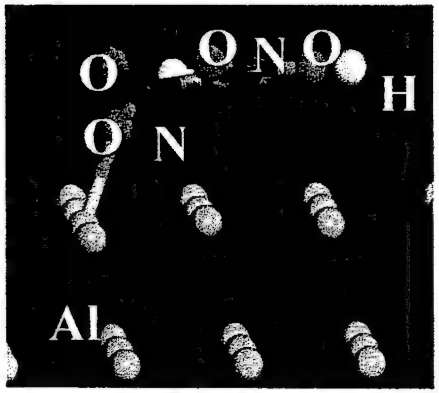
side view

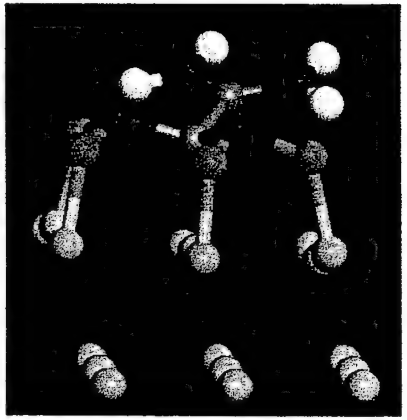
top view

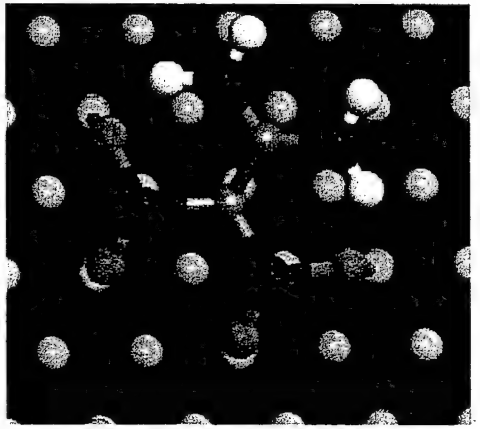












Formation of strong Al-O bonds; deformations of FOX-7

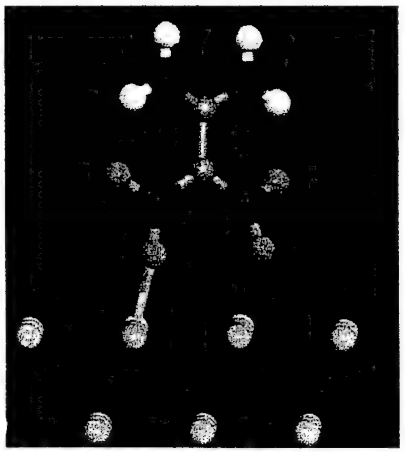
Dissociative Chemisorption of FOX-7

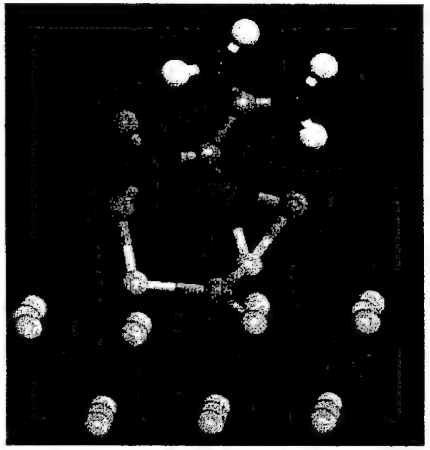
Initial configuration

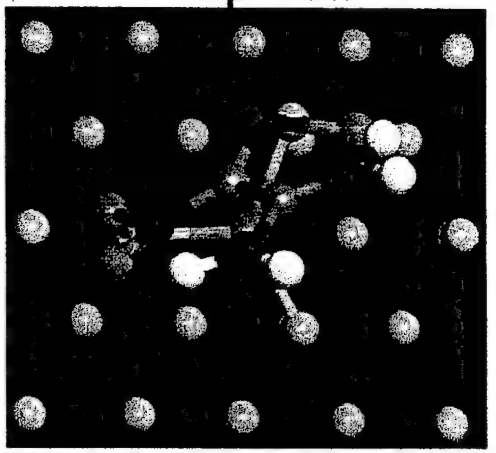
Optimized configuration

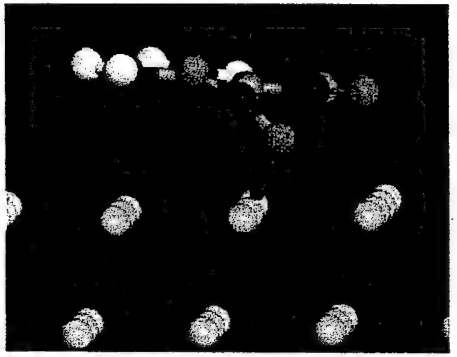
side view

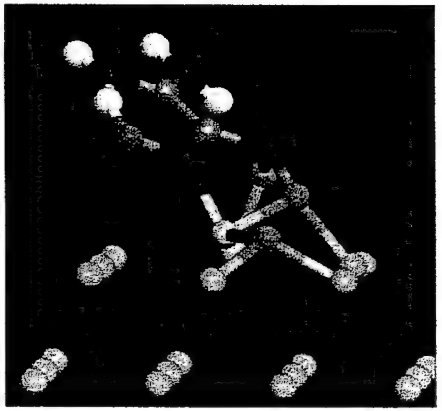
top view

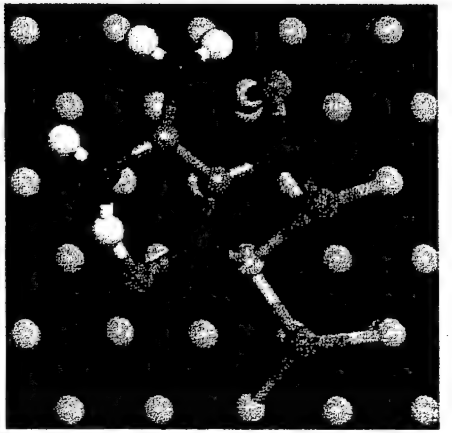












*** Dissociation of one O atom, oxidation of Al surface atoms.**

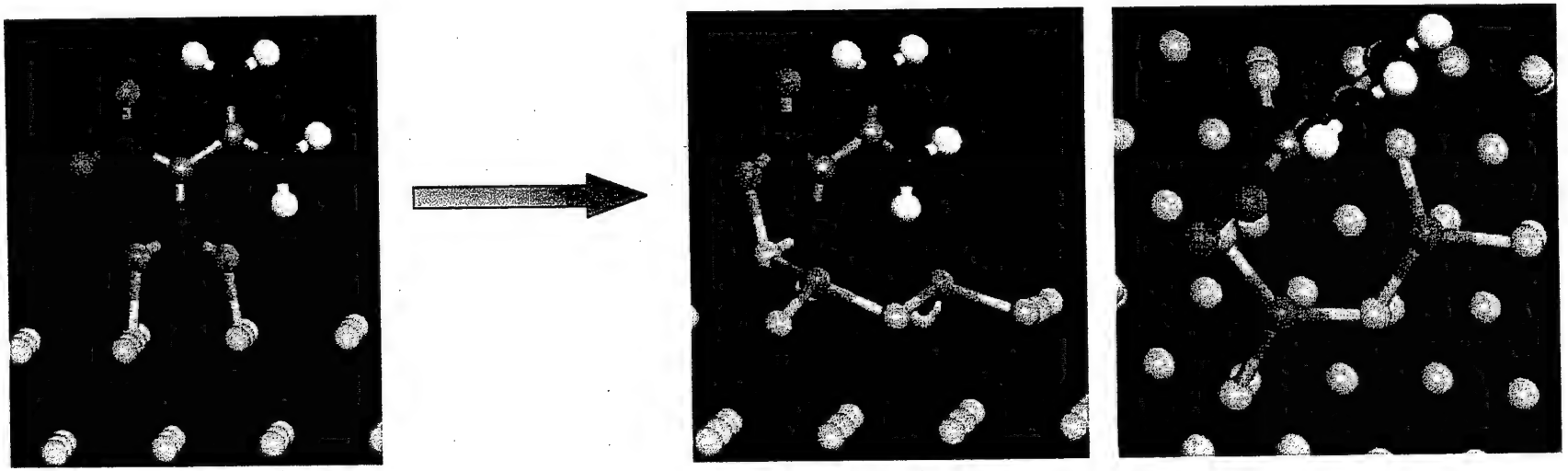
Dissociative Chemisorption of FOX-7

Initial configuration

Optimized configuration

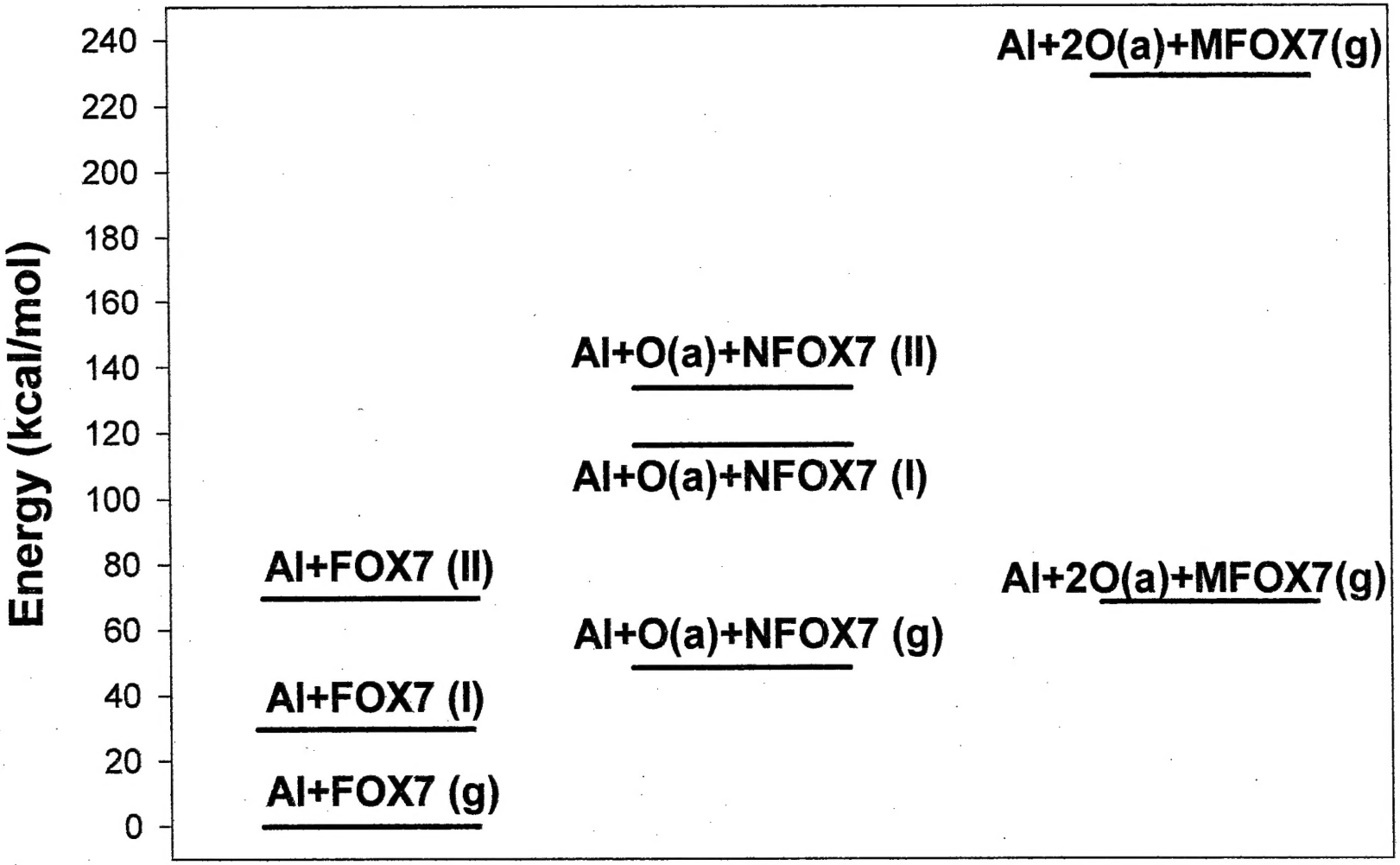
side view

top view



*** Dissociation of both O atoms, oxidation of Al surface atoms.**

Adsorption Energies of FOX-7



Computational requirements: 220,000 hours on ERDC Cray T3E, ARL SGI 3800

Conclusions

Both non-dissociative and dissociative interactions are found

(1) non-dissociative formation of N-O-Al bonds
(2) complete dissociation of one or two O atoms with subsequent formation of Al_3O "cap" sites.

Non-dissociative adsorption energies are 30-70 kcal/mol

Adsorption energies for single O-atom dissociation are 110-130 kcal/mol

Adsorption energies for double O-atom dissociation are 220-230 kcal/mol

Adsorption energies of the nitroso and nitrene fragments are 60-80 kcal/mol and 110-160 kcal/mol, respectively

Neither NM or FOX-7 completely passivate the aluminum surface against oxidation

Dissociative adsorption is competitive with O_2 adsorption (105 kcal/mol)

Chemisorption of nitroso and nitrene fragments may sterically and/or energetically inhibit growth of aluminum oxide overcoat

Formation of Al-O bonds appears to be general process in nitro compounds

Summary & Future Directions

Summary

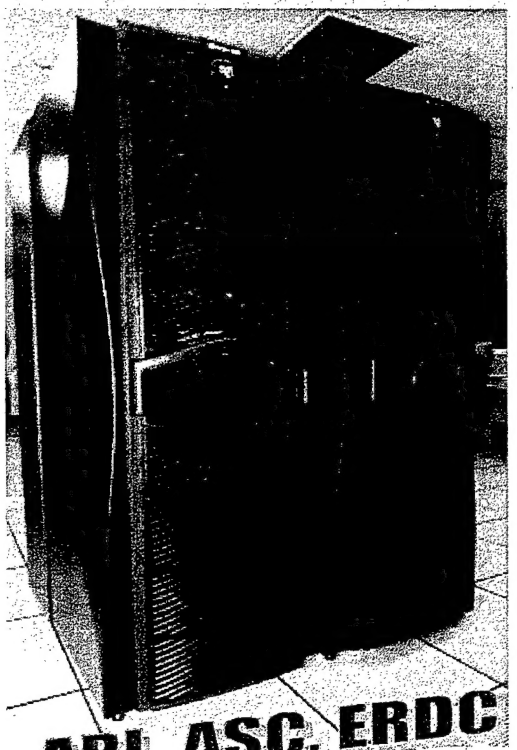
Interactions and adsorption energies of nitromethane and FOX-7 with the aluminum (111) surface have been calculated.

Multiple starting configurations have been examined (vertical & horizontal wrt metal surface; interactions with fcc, on-top, and hcp surface sites)

Future Directions

Interactions of NM and FOX-7 on aluminum oxide surface

Interactions of ammonium nitrate (AN) on Al (111)



ARL, ASC, ERDC
MSRCs

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DOD HPCMP

Challenge Project Award

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AFRL
AFOSR